



**Europäisches
Patentamt**

**European
Patent Office**

**Office européen
des brevets**

2 6. 11. 03

REC'D 0 4 DEC 2003

WIPO

PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02080272.4

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

Best Available Copy

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr:

Application no.: 02080272.4

Demande no:

Anmeldetag:

Date of filing: 13.12.02

Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Koninklijke Philips Electronics N.V.
Groenewoudseweg 1
5621 BA Eindhoven
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:

(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.

If no title is shown please refer to the description.

Si aucun titre n'est indiqué se référer à la description.)

Method of manufacturing a replica, as well as a replica obtained by carrying out
a UV light-initiated or thermal curing treatment of a reactive mixture

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)

Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

B29C/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SI SK

Method of manufacturing a replica, as well as a replica obtained by carrying out a UV light-initiated or thermal curing treatment of a reactive mixture

The present invention relates to a method of manufacturing a replica, which method comprises the provision of a curable resin composition between a mold and a substrate or a blank, carrying out a UV light-initiated or thermal curing treatment and removing the replica thus manufactured from the mold, which replica comprises the substrate and the reproduction of the mold provided thereon. The invention also relates to a replica
5 obtained by carrying out a UV light-initiated or thermal curing treatment of a reactive mixture or composition, especially a replica that has a high transparency for low wavelengths, i.e. 190-400 nm.

Replication molding techniques are well known. In such a technique, a replica
10 mold having a surface which is a negative copy of a surface of the final product is first prepared from a master mold. The final product is then molded against the negative surface of the replica mold, thus reproducing the surface configuration of the master mold.

Such a method is known per se from U.S. Patent No. 4,890,905, filed in the name of the current applicant. The replication process employs a mold or a matrix having an
15 accurately defined surface which is the negative of the desired optical profile of the replica. In the exact determination of the definition of the surface of the mold or matrix, the shrinkage of the synthetic resin of the replica must be taken into account. A small quantity of a liquid, curable synthetic resin composition is provided on the surface of the mold. The substrate, which may or may not be transparent to UV light, is subsequently pressed with the desired
20 side against the mold, or the mold is pressed against the substrate, as a result of which the synthetic resin spreads between the surface of the substrate and the surface of the mold. Said liquid, synthetic resin composition may be provided on the substrate instead of the mold. The synthetic resin mixture is cured and the substrate with the cured synthetic resin layer bonded thereto is removed from the mold. The free surface of the synthetic resin layer is the negative
25 of the corresponding surface of the mold. The advantage of the replication process is that optical components, such as lenses having a complicated refractive surface, for example an aspherical surface, can be manufactured in a comparatively simple manner without subjecting the substrate to complex polishing treatments. A drawback of such a replication by means of

polymerization is the occurrence of shrinkage. Particularly if the flow of the bondable resin composition is impeded by gelation or a substantial increase in viscosity due to the polymerization, further polymerization will lead to the development of stresses or even to premature delamination. If the product is subsequently removed from the mold, as in the case of, in particular, a replication process, only a partial relaxation of the stresses takes place, particularly if the product formed is composed of a densely bonded polymeric network. Such a bonded polymeric network is desired, however, for the cohesion of the product formed.

The criticality of the polymeric composition used to form replica molds has been confirmed by many unsuccessful attempts to obtain accurate replications of glass surfaces using a multitude of commercially available resins to form the replica molds.

For example, low-melting polyethylenes appear to form microscopic defects in the mold surfaces which reproduce in the final plastic lenses. Also, these materials are not believed to be sufficiently rigid and stiff to prevent distortion of the curing plastic lens. On the other hand, materials such as linear polymethyl methacrylate produce replica molds whose surfaces are solvent attacked by one of the materials primarily used in forming plastic lenses. A solvent attack of this nature produces a matte finish on the final plastic lens making it unsatisfactory.

Another property which makes some polymeric materials unacceptable is their release characteristics from the plastic lens being molded.

Basic optical properties such as high light transmittance, high refractive index, low residual birefringence after molding, and the like are required for geometrical optical lenses which are employed in various cameras such as common cameras, single use cameras, video cameras, and the like, optical recording units such as CD, CD-ROM, CD-Video, MO, CD-R, DVD, Blue Ray and the like, as well as OA equipment such as copiers, printers, and the like. In addition, general properties such as high thermal stability, high mechanical strength as well as hardness, low water absorption, high weather resistance, high solvent resistance, and the like are also required. Further, for production at low cost, excellent moldability is required.

An optical element having the aforementioned basic optical properties is known per se from U.S. Patent No. 6,285,513, comprising:

a silicon based resin satisfying following conditional formulas:

$$\frac{(\text{number of silicon atoms residing as } R_1\text{SiO}_{3/2} \text{ in the silicon based resin})}{(\text{total number of silicon atoms in the silicon based resin})} \geq 0,$$

(number of silicon atoms residing as $\text{SiO}_{4/2}$ in the silicon based resin)/(total number of silicon atoms in the silicon based resin) ≥ 0 ,

(number of silicon atoms residing as $\text{R1SiO}_{3/2}$ in the silicon based resin) +
(number of silicon atoms residing as $\text{SiO}_{4/2}$ in the silicon based resin} x 100/(total number of
5 silicon atoms in the silicon based resin) $\geq 10\%$

wherein R1 represents a hydrogen atom, a hydroxyl group, an amino group, a halogen atom or an organic group.

The optical elements comprised of the aforementioned curable silicon resins may be molded employing molding methods such as injection molding, extrusion molding,
10 pouring type molding and the like. In order to obtain the desired low birefringence, molding is preferably carried under no pressure application, if possible. As disclosed in the Examples the resulting silicone resin composition was injected into a lens molding dye at 40 atmospheric pressure and heated at about 150 °C. In the application of UV and deep-UV, disadvantage of the optical elements made in the aforementioned way may be that
15 transmission can be too low due to the long optical path through the component.

It is the objective of this invention to provide a method of manufacturing optical components through replication on a UV or deep-UV transparent glass, herewith greatly improving transmission for UV and deep-UV.

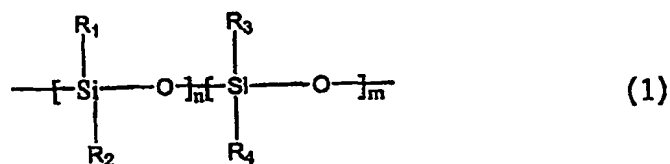
It is an object of the invention to provide a method of manufacturing a replica
20 wherein a reactive material having a sufficient transmission for UV and deep-UV is applied.

Another object of the invention is to provide a method of manufacturing a replica wherein a material is used that easily can be replicated and that is relatively insensitive to (deep) UV light.

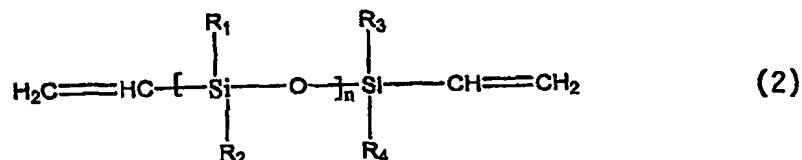
Yet another object of the invention is to provide a replica obtained by carrying
25 out a UV light-initiated or thermal curing treatment of a reactive compound, wherein a sufficiently good aspherical element is obtained.

The method mentioned in the opening paragraph is characterized in accordance with the invention that the resin composition used being a silicon based reactive material.

30 The resin composition according to the invention comprises

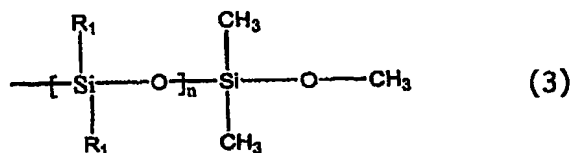


and

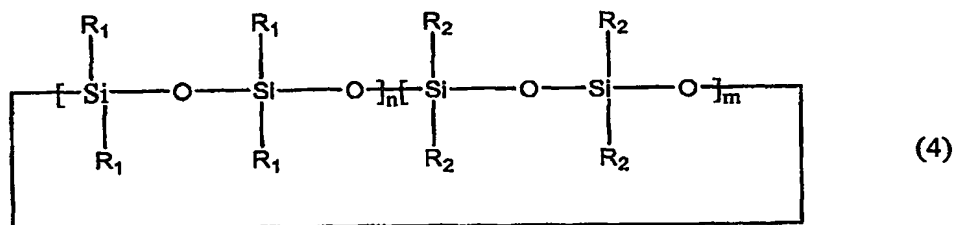


5 wherein $\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4$ = hydrogen, $\text{C}_2\text{-C}_{10}$ -alkyl, vinyl, phenyl, hydroxide, amino, halogen atom and at least one of $\text{R}_1, \text{R}_2, \text{R}_3$ and R_4 is hydrogen.

In a preferred embodiment of the present invention the resin composition further comprises



10 wherein $\text{R}_1, \text{R}_2, \text{R}_3$ and R_4 have the same meaning as already disclosed before. In addition it is preferred that the resin composition further comprises



wherein $\text{R}_1, \text{R}_2, \text{R}_3$ and R_4 have the same meaning as already disclosed before.

15 It is to be noted that the resin composition also comprises a metal catalyst, e.g. a platinum based catalyst, in an amount of 5-10 ppm Pt.

It is preferred that component (1) is present in an amount of 40-70 wt.%, based on the total weight of the curable resin composition.

In addition, it is preferred that component (2) is present in an amount of 15-40 wt.%, based on the total weight of the curable resin composition.

20

Furthermore it is preferred that component (3) is present in an amount of 10-30 wt.%, based on the total weight of the curable resin composition.

It is preferred that component (4) is present in an amount of 1.0-5.0 wt.%, based on the total weight of the curable resin composition.

5 The invention further relates to a replica obtained by carrying out a UV light-initiated or thermal curing treatment of a mixture comprising a silicon based reactive material, wherein the resin composition comprises the aforementioned components (1) and (2). Additional embodiments of the present invention are disclosed in the appending claims.

10 In order to obtain the aforementioned objects according to the invention the transparency of the replica obtained is at least 20%, when replicated on a glass material being transparent for the applied wavelength, measured at a thickness of 100 μm , an intensity of 100 $\mu\text{W}/\text{cm}^2$ and a wavelength of 190-400 nm, during a period of at least 50 hours.

15 In a preferred embodiment the transparency of the replica according to the invention is at least 90%, when replicated on a glass material being transparent for the applied wavelength, measured at a thickness of 100 μm , an intensity of 0.5 mW/cm^2 and a wavelength of 190-400 nm, during a period of at least 5000 hours.

The optical component obtained according to the invention is an (a)spherical lens, a lens array, a prism, a grating or another relief structure for optical applications, or a combination thereof, wherein the replica is characterized in that it is not birefringent.

20 These and other aspects of the invention will be apparent from and elucidated with reference to a preferred embodiment described hereinafter.

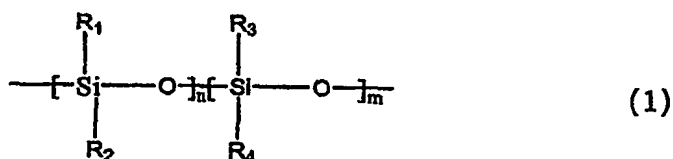
Example.

25 A hemispheric cylinder lens with a radius of 4 mm made of Sylgard 184 (trademark of Dow Chemicals, a mixture of components (1)-(4)) has a wavelength of 257 nm and an intensity of 500 $\text{microWatt}/\text{cm}^2$, an initial transmission of only 5% which decreases within several hours to below 1%. A layer of 100 micron of the same material replicated on UV transparent quartz lens results in an optical element which at the same dose and wavelength has a transmission of 80% over a period of several days.

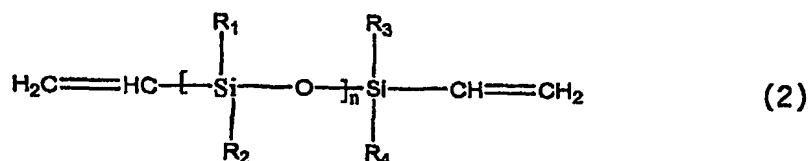
CLAIMS:

1. A method of manufacturing a replica, which method comprises the provision of a curable resin composition between a mold and a substrate or a blank, carrying out a UV-light initiated or thermal curing treatment and removing the replica thus manufactured from the mold, which replica comprises the substrate and the reproduction of the mold provide thereon, characterized in that, the resin composition used being a silicon based reactive material.

2. A method as claimed in claim 1, characterized in that the resin composition comprises

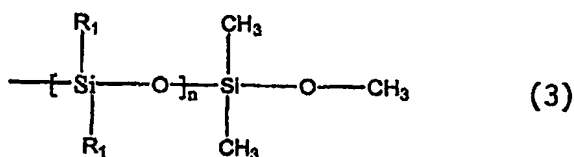


and



wherein $\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4$ = hydrogen, $\text{C}_2\text{-C}_{10}$ -alkyl, vinyl, phenyl, hydroxide, amino, halogen atom, and at least one of $\text{R}_1, \text{R}_2, \text{R}_3$ and R_4 is hydrogen.

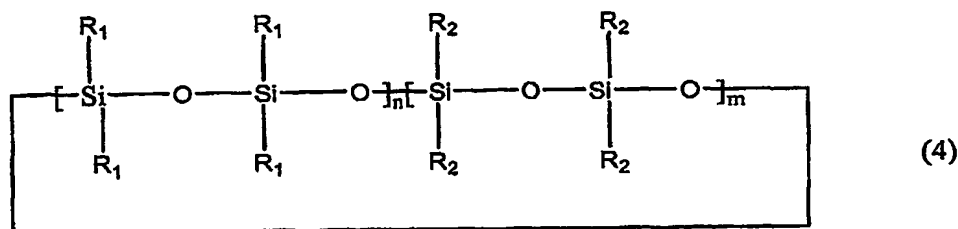
3. A method as claimed in claim 2, characterized in that the resin composition further comprises



wherein R_1 , R_2 , R_3 and R_4 have the same meaning as disclosed in claim 2.

4. A method according to claims 2-4, characterized in that the resin composition further comprises

5



wherein R_1 , R_2 , R_3 and R_4 have the same meaning as disclosed in claim 2.

- 10 5. A method according to claims 2-4, characterized in that component (1) is present in an amount of 40-70 wt.%, based on the total weight of the curable resin composition.

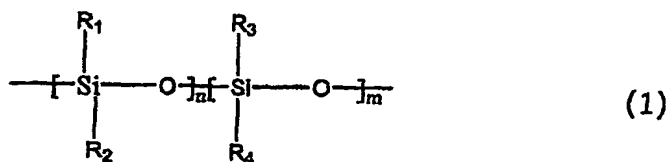
- 15 6. A method according to claims 2-5, characterized in that component (2) is present in an amount of 15-40 wt.%, based on the total weight of the curable resin composition.

- 20 7. A method according to claims 2-6, characterized in that component (1) is present in an amount of 10-30 wt.%, based on the total weight of the curable resin composition.

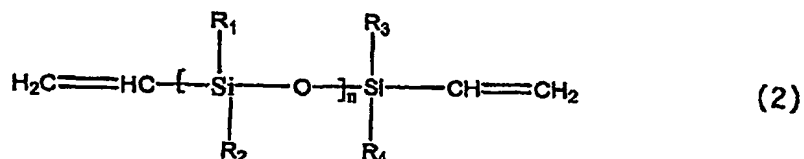
- 25 8. A method according to claims 2-7, characterized in that component (4) is present in an amount of 1.0-5.0 wt.%, based on the total weight of the curable resin composition.

9. A replica obtained by carrying out a UV light-initiated or thermal curing treatment of a mixture comprising a silicon based reactive material.

- 30 10. A replica as claimed in claim 9, characterized in that the silicon based reactive material comprises

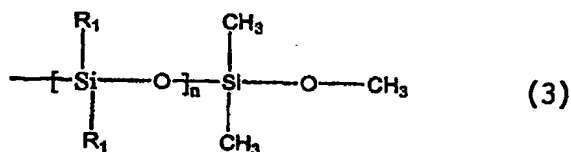


and



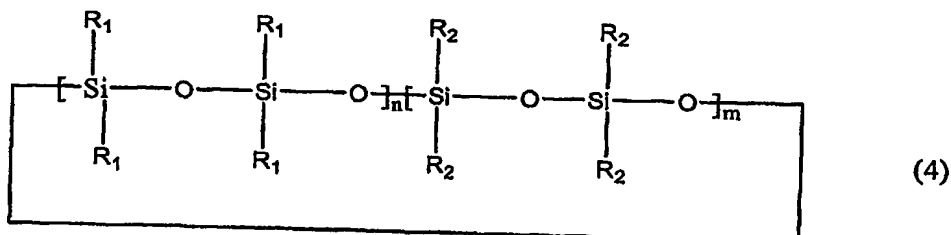
- 5 wherein $\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4$ = hydrogen, $\text{C}_2\text{-C}_{10}$ -alkyl, vinyl, phenyl, hydroxide, amino, halogen atom, and at least one of $\text{R}_1, \text{R}_2, \text{R}_3$ and R_4 is hydrogen.

11. A replica as claimed in claim 10, characterized in that the silicon based reactive material further comprises



10 wherein $\text{R}_1, \text{R}_2, \text{R}_3$ and R_4 have the same meaning as disclosed in claim 10.

12. A replica as claimed in claims 10-11, characterized in that the silicon based reactive material further comprises



15 wherein $\text{R}_1, \text{R}_2, \text{R}_3$ and R_4 have the same meaning as disclosed in claim 10.

13. A replica as claimed in claims 9-12, characterized in that its transparency is at least 20%, when replicated on a glass material being transparent for the applied wavelength,

measured at a thickness of 100 μm , an intensity of 100 $\mu\text{W}/\text{cm}^2$ and a wavelength of 190-400 nm, during a period of at least 50 hours.

14. A replica as claimed in claims 9-13, characterized in that its transparency is at least 90 %, when replicated on a glass material being transparent for the applied wavelength, measured at a thickness of 100 μm , an intensity of 0.5 mW/cm^2 and a wavelength of 190-400 nm, during a period of at least 5000 hours.
15. A replica as claimed in claims 9-14, characterized in that it is not birefringent.
16. A replica as claimed in claims 9-15, characterized in that the replica obtained is an optical component.
17. A replica as claimed in claim 16, characterized in that the optical component obtained is an (a) spherical lens, a lens array, a prism, a grating or another relief structure for optical applications, or a combination thereof.

ABSTRACT:

The present invention relates to a method of manufacturing a replica, which method comprises the provision of a curable resin composition between a mold and a substrate or a blank, carrying out a UV light-initiated or thermal curing treatment and removing the replica thus manufactured from the mold, which replica comprises the substrate and the reproduction of the mold provided thereon. The invention also relates to a replica
5 obtained by carrying out a UV light-initiated or thermal curing treatment of a reactive compound, especially a replica that has a high transparency for low wavelengths, i.e. 190-400 nm.

PCT Application

IB0305435



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☒ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.